Optical and EPR Studies on the 5 eV Band of CdCl Crystals (Special Issue on Physical, Chemical and Biological Effect of Gamma Radiation, XIII)

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Optical and EPR Studies on the 5 eV Band of $CdCl_2$ Crystals

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Optical absorption spectra of various impurity ions doped in $CdCl_2$ crystals are studied to identify the center responsible to the 5 eV absorption band. Electron paramagnetic resonance absorption spectra are also investigated on the γ-ray or x-ray irradiated $CdCl_2$ crystals.

The crystals can be classified into two groups: (1) $CdCl_2$ containing Li ions and (2) $CdCl_2$ containing other impurities than Li ions. The 5 eV absorption band of group 1 crystals appeared at about 0.10~0.16 eV lower energy than that of group 2 crystals. In the crystals of group 1, the 5 eV absorption band disappeared with the irradiation of γ-rays or x-rays at room temperature and paramagnetic center was produced instead. In the crystals of group 2, the irradiation of γ-rays of x-rays at room temperature did not make any change in the 5 eV absorption band but the irradiation of x-rays at liquid nitrogen temperature caused the decrease of the intensity of the 5 eV absorption and an appearance of a small new absorption band at 4.55 eV. After the irradiation had ceased the recovery of the 5 eV absorption and the disappearance of 4.55 eV band were attained very quickly.

Some discussions are made on the possible models of the center responsible to the 5 eV band and the paramagnetic center.

I. INTRODUCTION

There are considerably many investigations on the electronic states of metal impurities in the $CdCl_2$ type or CdI_2 type crystals with the methods of electron paramagnetic resonance absorption, optical absorption and emission of light.[1~11]

Some studies have also been reported on the change of these electronic states brought by the irradiation of γ-rays or x-rays.[12,13]

In general, any dominant absorption bands are not observed at the lower energy side of the fundamental absorption, which rises about 5.5 eV, down to the near infra-red region in the optical absorption spectra of undoped $CdCl_2$ crystals. Sometimes, an absorption band is observed in the vicinity of the photon energy of 5 eV in the optical absorption spectra of $CdCl_2$ crystals doped with certain monovalent metal ions or doped without any intended impurities.

Though the appearance of this absorption band seems to be almost independent from the kind of doped monovalent metal ions, it may be due to the processes of drying the raw chemicals prior to the growth of single crystals or to some unintended impurities in the $CdCl_2$.

It is natural to consider that the center of this absorption band may have

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important relation to a impurity which remains unrejected in the $CdCl_2$ chemicals during the crystal growth, to a miner impurity contained in the added chemicals to $CdCl_2$ as intended impurities or to an ion such as hydroxide oxygen or nitrogen which comes to be mixed into $CdCl_2$ during dehydration and baking processes of raw chemicals of crystals in the low vacuum.

It has been reported that in alkali halides there exist some optical absorption bands due to the hydrogen atoms, hydroxide ions or oxide molecular ions which are brought into crystals during the preparation processes of single crystals or converted from them by irradiation. They have the electronic absorption peaks near the fundamental absorption of the host crystals and their spectroscopic characteristics have been investigated extensively.[14~17]

For the investigation of irradiation effects on $CdCl_2$ crystals or on the impurities in the $CdCl_2$ crystals, the role of the center responsible to the 5 eV band cannot be neglected as they may act as sources or traps for electrons or holes.

It may be interesting to study the characteristics of this band to clarify the origin of it. It may also be important to make researches on the relation of the center of this band to other impurities or to the irradiation effects on the crystals.

In this paper absorption spectra of $CdCl_2$ doped with various impurities are reported and the relations between the 5 eV band and impurities doped into the $CdCl_2$ crystals are described.

EPR and optical absorption studies on the relations between the center of the 5 eV band and doped impurities under the irradiation of γ-rays or x-rays are also reported and some discussions on the origin of the center of the 5 eV band are given here.

II. EXPERIMENTAL AND RESULTS

II. 1. Sample Preparation

The drying procedure of chemicals was as follows: the mixture of reagent grade $CdCl_2$ and chemicals to be doped as an impurity was heated in the vacuum of about 10^{-3} mmHg at 80°C for a few hours and heated at 500°C for one or two hours further. The drying procedure of samples containing KCl or TlCl as an impurity was not such as described above. They were melted in the vacuum of 10^{-3} mmHg to remove water and other adsorbed gases.

These dried chemicals were sealed in the quartz crucible in the vacuum and used to grow the single crystal of $CdCl_2$ by Stockbarger method. The quartz crucible was pulled down with the rate of 15°C per hour in the furnace.

The impurities doped were LiCl, LiOH, KCl, TlCl, $Cd(OH)_2$, CdO, $CaCl_2$, $ZnCl_2$, $PbCl_2$, $MnCl_2$, $CuCl_2$ and $CrCl_3$.

II. 2. Optical Absorption Spectra

The samples of about 10 mm × 5 mm × 0.2 mm size were cloven from crystalline ingot for optical absorption measurements. The crystal has layer structure

and the direction of incident light for absorption measurements was parallel to the crystal *c*-axis which is perpendicular to the layer plane.

II. 2.1. Undoped $CdCl_2$

Optical absorption spectra of pure $CdCl_2$ are shown in Fig. 1.

Sometimes a weak absorption peak appeared at 5.02 eV, while it scarcely appeared in the spectra of well baked pure crystals.

An absorption peak at 5.68 eV was also found at liquid nitrogen temperature. As it overlapped on the rising slope of the fundamental absorption and the surface of the crystal was apt to become dim because of the hygroscopic nature of the crystal, it was very difficult to distinguish the peak from the fundamental absorption. Any clear relation between 5.68 eV band and 5.02 eV band is not apparent.

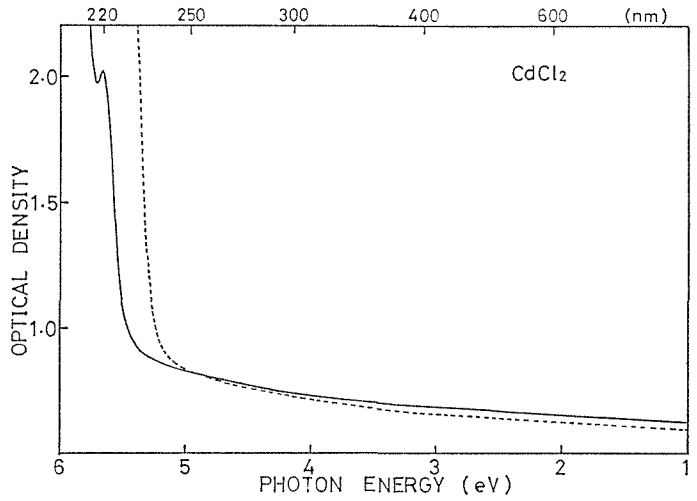

Fig. 1. Optical absorption spectra of undoped $CdCl_2$.
Dotted curve was measured at room temperature and solid curve was measured at liquid nitrogen temperature.

II. 2.2. $CdCl_2$: LiCl and $CdCl_2$: LiOH

Optical absorption spectra of $CdCl_2$: LiCl and $CdCl_2$: LiOH are shown in Fig. 2(a) and (b) respectively. They resemble each other. In the measurement at room temperature there existed an absorption band with the peak at 4.95 eV and the half width of 0.36 eV for each crystal. The band peak shifted to 5.00 eV and the band width diminished to 0.31 eV at 77°K.

This means that the center of this absorption has considerable interaction with the neighboring crystal lattices.

It is clear that the peak position of this band differs not only from 5.02 eV peak of undoped $CdCl_2$ but also from 5.05~5.03 eV peak of $CdCl_2$: $Cd(OH)_2$, $CdCl_2$: CdO and $CdCl_2$ doped with other impurities than lithium as described below.

The intensity of 4.95 eV absorption differed from sample to sample which

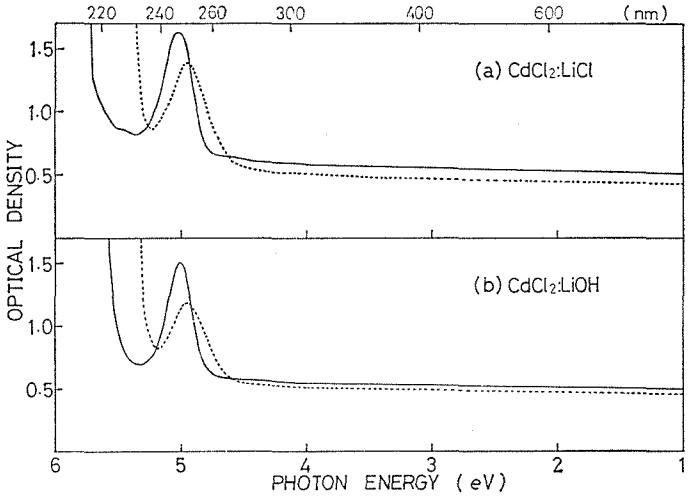

Fig. 2. Optical absorption spectra of group 1 $CdCl_2$ crystals.
(a) $CdCl_2$: LiCl. (b) $CdCl_2$: LiOH.
Dotted curves were measured at room temperature and solid curves were measured at liquid nitrogen temperature.

was cloven from different part of a crystalline ingot. The stronger absorption was observed for the samples cloven from upper part of the $CdCl_2$: LiOH ingot which had been grown by pulling down the crucible in the furnace.

This implies that wheather the specific gravity of the center is comparatively small in the melt or the segregation constant of the center has a small value in the $CdCl_2$: LiOH.

An absorption band at 5.7 eV was also observed at 77°K in the $CdCl_2$: LiCl spectra.

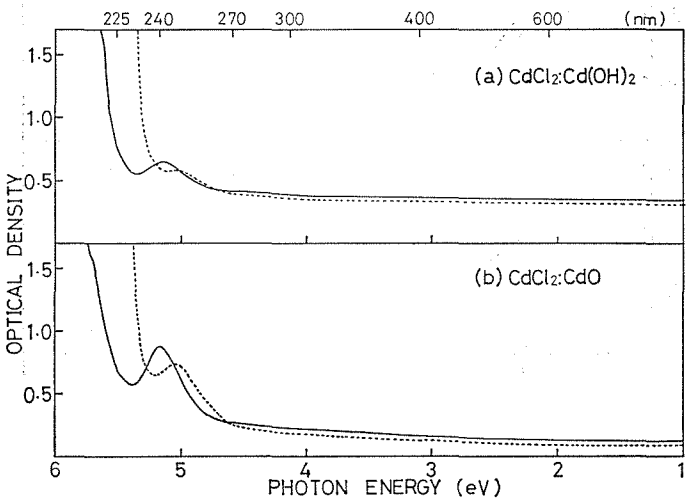

Fig. 3. Optical absorption spectra of (a) $CdCl_2$: $Cd(OH)_2$ and (b) $CdCl_2$: CdO. Dotted curves and solid curves were measured at room and liquid nitrogen temperatures respectively.

II. 2.3. $CdCl_2 : Cd(OH)_2$ and $CdCl_2 : CdO$

Optical absorption spectra of $CdCl_2 : Cd(OH)_2$ and $CdCl_2 : CdO$ are shown in Fig. 3(a) and (b) respectively. Both spectra resemble each other.

Absorption bands were observed at 5.05 eV ($CdCl_2 : Cd(OH)_2$) and 5.03 eV ($CdCl_2 : CdO$) and the half widths of both bands were 0.37 eV at room temperature. The band peaks shifted to 5.16 eV and the band widths diminished to 0.33 eV at 77°K.

Samples cloven from upper part of the $CdCl_2 : Cd(OH)_2$ showed stronger absorption.

The energies of these absorption bands are apparently higher than that of $CdCl_2$ containing lithium.

The Li^+ ion in the crystal seems to perturb the electronic state of the center resposible to the 5 eV band and to make its absorption peak shift to the lower energy.

Any splitting or fine structure of the band was not observed at room temperature or 77°K.

The 5.68 eV band was also observed. The separation of this band from the fundamental absorption was not sufficient to make the comparison of this band with the corresponding band of crystals with lithium.

II. 2.4. $CdCl_2$ with other impurities

Sometimes an absorption band has been observed near the threshold of the fundamental absorption in the $CdCl_2$ single crystals containing KCl or TlCl. The optical absorption spectra are shown in Fig. 4.

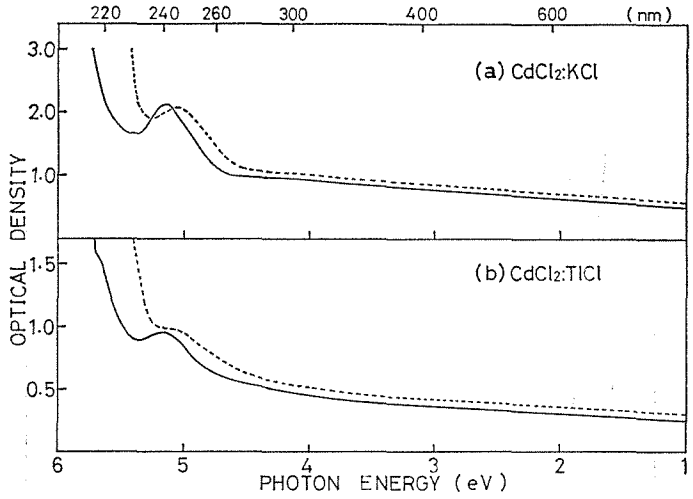

Fig. 4. Optical absorption spectra of (a) $CdCl_2 : KCl$ and (b) $CdCl_2 : TlCl$ measured at room temperature.

Each spectrum shows very similar absorption to that of $CdCl_2 : Cd(OH)_2$ and $CdCl_2 : CdO$.

$CdCl_2$ single crystals doped with other impurities such as $MnCl_2$, $CaCl_2$ or

$ZnCl_2$ had not any absorption band other than the fundamental absorption in the energy ranges of ultra-violet, visible and near infra-red.

Though $CdCl_2$ single crystals doped with $CuCl_2$, $PbCl_2$ or $CrCl_3$ had some remarkable absorption bands as shown in Fig. 5, the corresponding absorption to the 5 eV band was not observed near the threshold of the fundamental absorption.

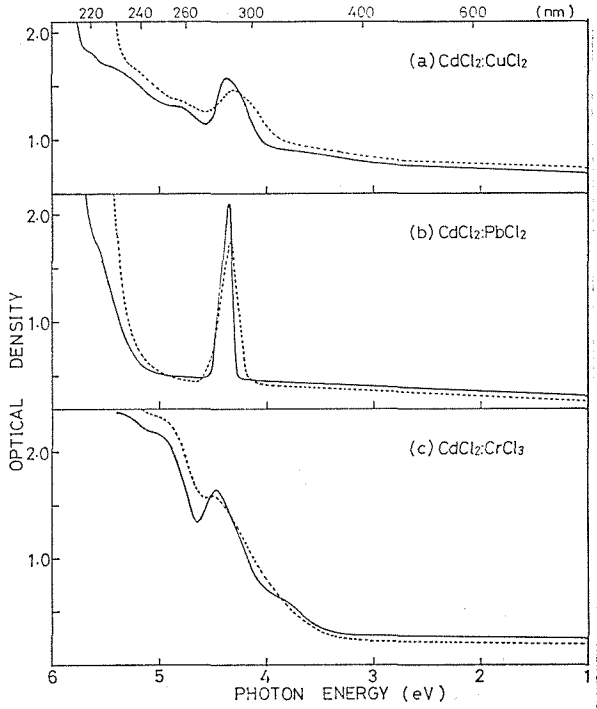

Fig. 5. Optical absorption spectra of (a) $CdCl_2 : CuCl_2$, (b) $CdCl_2 : PbCl_2$ and (c) $CdCl_2 : CrCl_3$.
Dotted curves and solid curves were measured at room and liquid nitrogen temperatures respectively.

II. 3. Irradiation Effects on the Optical Absorption Spectra

The effects of γ-ray or x-ray irradiation on the optical absorption spectra have been investigated for undoped $CdCl_2$, $CdCl_2 : LiCl$, $CdCl_2 : KCl$, $CdCl_2 : LiOH$, $CdCl_2 : Cd(OH)_2$ and $CdCl_2 : CdO$ single crystals.

Samples can be classified into two groups according to the effects of irradiation. Group 1 crystals contain lithium impurities and group 2 crystals do not contain lithium impurities.

The effects of γ-ray or x-ray irradiation for each group are described below.

(i) Group 1 crystals

Any change was not observed in the 5 eV absorption band by the irradiation of γ-rays of Co^{60} with the dosage of 2×10^7 R on the crystals at liquid nitrogen temperature.

When the irradiation of γ-rays on the crystals was made at room tempera-

ture, the 5 eV band disappeared completely with a dosage of 3×10^6 R and a very broad band appeared near 3 eV. The intensity of the broad band increased as the dosage of γ-rays increased even after the 5 eV band had vanished.

This suggests that the center responsible to the 5 eV band is not transformed directly into the center responsible to the broad band near 3 eV.

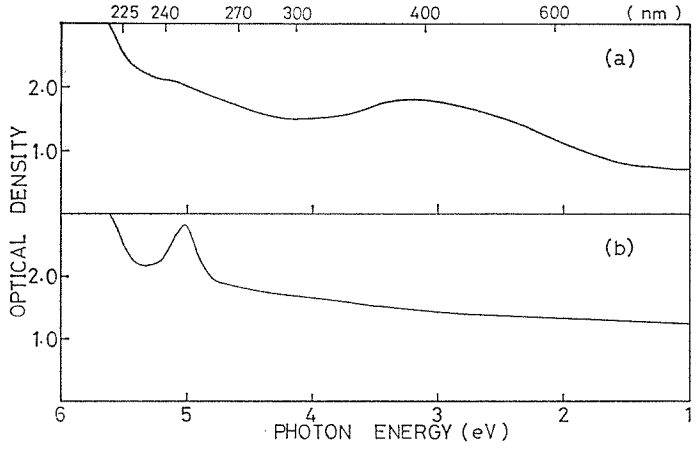

Fig. 6. Absorption spectra of $CdCl_2$: LiCl.
(a) Irradiated at room temperature with γ-ray dosage of about 3×10^6 R.
(b) Irradiated at liquid nitrogen temperature with γ-ray dosage of about 2×10^7 R.
Absorption measurements were made at liquid nitrogen temperature.

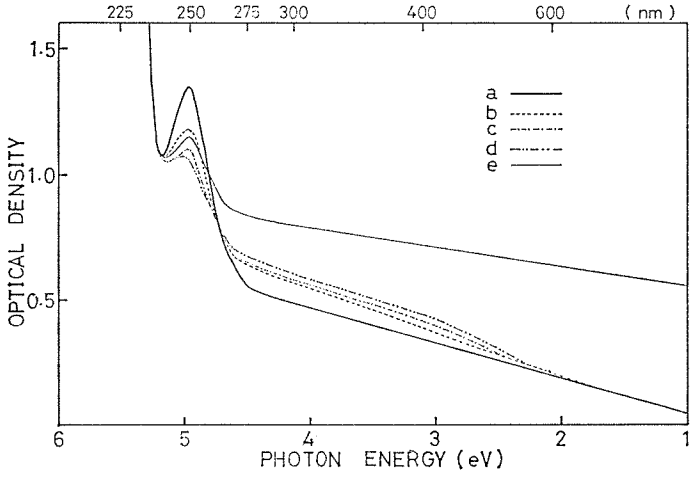

Fig. 7. Optical absorption spectra of x-ray irradiated $CdCl_2$: LiOH.
(a) Spectrum prior to the x-ray irradiation.
(b) Spectrum irradiated with x-ray for 60 minutes.
(c) Spectrum irradiated with x-ray for 120 minutes.
(d) Spectrum irradiated with x-ray for 180 minutes.
X-ray irradiation was made at room temperature with Toshiba AFX 60 A x-ray tube operating at 40 KV and 25 mA.
(e) Recovered spectra of the x-ray irradiated $CdCl_2$: LiOH measured at 9 days after the irradiation.

Other new absorption bands were not observed after the irradiation of γ-rays at room temperature.

Absorption spectra of γ-ray irradiated $CdCl_2$: LiCl crystals are shown in Fig. 6. Spectrum (a) was obtained by irradiating the crystal at room temperature and (b) at liquid nitrogen temperature.

As described later, an electron paramagnetic resonance absorption was observed for the crystals of group 1 irradiated at room temperature.

The intensity of the 5.01 eV absorption band of $CdCl_2$: LiOH decreased and the absorption between 4.5 eV and 2.5 eV increased as the dosage of x-ray irradiation was increased at room temperature.

When the x-ray irradiated $CdCl_2$: LiOH at room temperature was kept in the dark vacuum for 9 days after irradiation, the 5.01 eV band recovered to a certain extent and the absorption between 4.5 eV and 2.5 eV decreased. This is shown in Fig. 7.

(ii) Group 2 crystals

The precise peak positions of the 5 eV absorption appeared at higher energies for the crystals of group 2 than for that of group 1.

The crystals of group 2 differ from that of group 1 also in the effects of γ-ray irradiation or x-ray irradiation.

The intensity of the 5.16 eV band of $CdCl_2$: CdO decreased with x-ray irradiation at 77°K and a new absorption band appeared at 4.55 eV. This band disappeared within a few minutes after the irradiation had ceased at 77°K and the 5.16 eV band recovered completely.

No change was observed in the 5 eV absorption band for $CdCl_2$: $Cd(OH)_2$ and $CdCl_2$: KCl with the irradiation of γ-rays of 5×10^7 R at room temperature.

II. 3. Electron Parmagnetic Resonance Absorption Spectra

$CdCl_2$ samples showed the EPR spectra of Mn^{2+} ions which might remain in the host crystals.

Though the 5 eV absorption band of $CdCl_2$ doped with LiCl disappeared com-

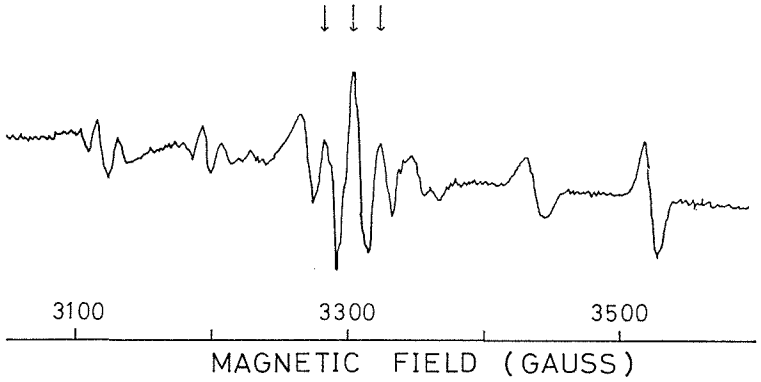

Fig. 8. EPR absorption spectra of γ-ray irradiated $CdCl_2$: LiCl.
A spectrum of Mn^{2+} ion is superposed on the three lines produced by γ-ray irradiation. γ-ray irradiation was made at room temperature.

pletely with the γ-ray irradiation of 3×10^6 R at room temperature, new absorption lines appeared in the EPR spectra besides that of Mn^{2+} ions in the crystal. The new EPR spectra are composed of three lines as shown in Fig. 8. The value of g-factor of the central line is 2.011, the intensity ratio of three lines is about 1 : 3 : 1, the separations of lines are about 20 gauss and the peak to peak width of a line is about 10 gauss each at 77°K.

Any anisotropy of EPR spectrum was not observed with respect to the directions of static magnetic field and crystal orientation.

The EPR spectra of Mn^{2+} ions in the host crystal seemed to make no change with the irradiation of γ-rays.

III. DISCUSSION

As for the positions of the absorption peaks, the 5 eV band of $CdCl_2$ crystals which appears at the edge of the fundamental absorption resembles the absorption bands due to $(OH)^-$ ions[15,16], O_2^- ions[14] or O^{2-} ions[17] in the alkali halide crystals.

It is well known that these ions are apt to be mixed into crystals during the procedure of preparation and growth. The possibility that the 5 eV band of $CdCl_2$ crystals is due to these ions cannot be eliminated at this stage.

The absorption peak of the 5 eV band shifts to the higher energy and the width of the band decreases and becomes sharp at lower temperature. This suggests that the electrons responsible to the absorption band would suffer the considerable influence of the potential energy of surrounding lattices. This situation is similar to that of F band, α band and β band in alkali halide crystals.[18,19]

The absorption peak of the 5 eV appears at 0.15 eV lower for the group 1 crystals than for the group 2 crystals. This implies that the center is stable in the position close to Li^+ impurity in the crystals and the center suffers a strong perturbation from neighboring Li^+ ion. This is very similar to the case of F_A center in alkali halide crystals, however, the splitting of the band is not observed in this case in contrast with the F_A band in alkali halide crystals.[20]

Though the irradiation of γ-rays or x-rays on the group 1 crystals does not make any change in the 5 eV band at liquid nitrogen temperature, the 5 eV band can be vanished completely by the irradiation on the group 1 crystals at room temperature. The irradiation on the group 2 crystals does not make any change in the 5 eV band at room temperature.

These facts suggest that the 5 eV band does not owe to the fundamental absorption perturbed by the impurities or imperfections accompanied by the impurities as the case of α band or β band in the alkali halide crystals.[18]

It is natural to consider that the disappearance of the 5 eV band results from the destruction of the centers caused by the release of lithium from the centers. Li^+ ions capture electrons released from the centers or from other ions by the action of ionizing radiation and become neutral lithium atoms. They may leave the centers and move around in the crystals to make aggregations of lithium

metals. The broad absorption band around 3.5 eV of group 1 crystals may be attributed to these lithium aggregations.[21~23]

Though irradiation of γ-rays or x-rays on the group 2 crystals at room temperature does not affect the 5 eV absorption bands, intensity of the 5 eV band decreases and new absorption band appears with the irradiation of x-rays on $CdCl_2$: CdO of the group 2 at 77°K. This new band is very unstable and vanishes in few minutes at 77°K and the intensity of the 5 eV band recovers.

In group 2 crystals, a certain temporary change caused by the irradiation is not accompanied with the release of lithium or other ions from the center and the destruction of the center does not occur. To the contrary, in group 1 crystals the change caused by the irradiation at room temperature is accompanied with the release of lithium from the center and destruction of the center, so that the recovery of the crystal from the radiation damage is very slow and incomplete.

Finally, the 5 eV absoption band may belong to an intra radical transfer spectrum of impurity radical such as $(OH)^-$ or O_2^- in the crystal or to a kind of charge transfer spectra due to a transfer of an electron from an unknown impurity to its ligand or from the ligand to the impurity where the ligand contains Li^+ ion in the case of group 1 crystal.

Some possible models will be discussed below for the paramagnetic centers produced by γ-ray irradiation in the group 1 crystals.

Three unequal lines in the EPR spectra such as shown in Fig. 8 can be produced in the following cases. (1) Superhyperfine structure of an electron or a hole interacting with two similar nuclei whose spin quantum number are 1/2. (2) Superposition of a single line caused by an isolated one electron or one hole center and three lines caused by a pair of two similar one electron or one hole certers coupled by an exchange interaction. (3) EPR spectrum of an ion whose electronic spin quantum number is 3/2 and orbital angular momentum of the ground state is quenched. (4) Superposition of hyperfine structures of isotopes with different nuclear spin quantum numbers.

As case (1), nuclei H^1, Cd^{111} and Cd^{113} would be plausible and as case (2), O_2^- ions would be considered. As there may exist sufficiently large anisotropies in the interactions between these two nuclei or two centers in the crystals, certain anisotropies may be expected in the EPR spectra. This contradicts the experimental observations. As a strong hyperfine interaction of Li^7 may exist, the possibility of the appearance of a single line due to the colloidal aggregates of lithium metal[24] and three lines or more due to the exchange interactions between neutral lithium atoms in the aggregates should be examined in detail.

As for the case (3), firstly, iron group ions of $(d)^3$ or $(d)^7$ electronic configurations can be considered. In this case these paramagnetic centers would have been converted from the centers responsible to the 5 eV optical absorption bands. Cr^{3+}, $(3d)^3$, ion may be converted from Cr^{2+}, $(3d)^4$, by irradiation. Though Cr^{3+} ion in the $CdCl_2$ shows complex optical absorption spectra as shown in Fig. 5 (c), irradiated crystals of group 1 do not show such absorption bands, so that Cr^{3+} ion can be excluded from the model of the paramagnetic center.

As Co^{2+}, $(3d)^7$, ion has a large number of hyperfine structures and large values

of g-factor[3], this ion is also excluded.

If it is assumed that Ni^{3+}, $(3d)^7$, can be converted from Ni^{2+}, $(3d)^8$, the optical absorption spectrum of Ni^{2+} ion in $CdCl_2$ has been known[8] and the 5 eV absoption band has not been observed in the spectrum, then Ni^{3+} ion also can be excluded for the center.

Secondly, as O^+ ion has an electronic configuration $(3p)^3$ and ^4S ground state, it would have three EPR absorption lines and g values of about 2. The calculated intensity ratio of the lines is 3 : 4 : 3, in the strong magnetic field approximation. Agreement of this ratio with observed one is not good.

As for the possibility of (4), isotopes responsible to the spectrum must have nuclear spin quantum numbers of 1/2 and zero with the abundance ratio of about 2 to 3 or nuclear spin quantum numbers of 1 and zero with the abundance ratio of about 3 to 2. There may exist none of natural isotope satisfying these limitation except cadmium.

Cadmium has many isotopes, though Cd^{111} and Cd^{113} have nuclear spins of 1/2 and abundance of 12.8 percent and 12.3 percent respectively, Cd^{112} and Cd^{114} have no nuclear spins and abundance is 24.1 percent and 28.9 percent respectively. The abundance ratio is not satisfactory to explain the observed intensity ratio of the lines.

After all, a decisive model is not obtained at this stage and colloidal lithium, oxygen ion (O^+) or cadmium ion (Cd^{3+} or Cd^+) is not excluded from the model of the paramagnetic center.

More extensive studies are needed under various conditions in irradiation dosage and temperature and in sample preparation to obtain the compatible explanation for the optical and EPR data.

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